INVESTIGATION OF THE HEAT RESISTANCE OF ST-4 TITANIUM ALLOY AND CERTAIN PROTECTIVE COATINGS ON IT

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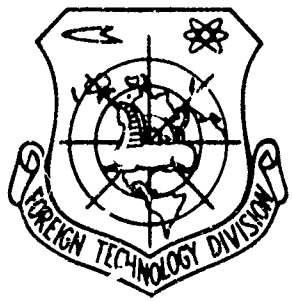

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13 ABSTRACT

A kinetic and structural investigation was carried out of the oxidizability in the temperature interval of 700-1000 C of the ST-4 titanium alloy, unprotected and protected by coatings based on Si and Mo-Si. The Si coating consisted mainly of the compound Ti_5Si_3 and TiSi and $TiSi_2$ traces; the Mo-Si coating consisted mainly of $MoSi_2$ and of Mo_5Si_3. The Ti_5Si_3 coating showed the best protective properties against gaseous corrosion at 800-1000 C. The heat resistance of the ST-4 alloy coated with Ti_5Si_3 at 800 C was 70 times greater than the heat resistance of the 80% Ni + 20% Cr alloy. Protection of the ST-4 alloy by the investigated coatings makes it possible to eliminate the negative influence on the oxidation rate of titanium and its alloys of effects of the high solubility of oxygen (and nitrogen) in them and of the A to B transformation. [AP1205762]

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	ROLE	WT	ROLE	WT	ROLE	WT
Titanium Alloy Alloy Designation Silicide Molybdenum Compound Titanium Compound Protective Coating Heat Resistance/(U)ST-4 Titanium Alloy						

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A structural-kinetic investigation has been conducted in the 700-1000°C temperature range concerning the oxidizability of ST-4 alloy, both protected and unprotected with coatings having a Si and MoSi base. Protection of the alloy with the coatings under study enables us to eliminate the negative influence on the oxidation rate of titanium and its alloys of the effects of high soluability of oxygen (and nitrogen) in them, and $\alpha \rightarrow \beta$ transformations.

A silicon coating, Ti_5Si_3 in the initial phase, is the best protection against gas corrosion at 800-1000°C. The heat resistance of the alloy with this coating at 800°C is approximately 70 times higher than for an alloy consisting of 80% Ni and 20% Cr, while at 1000°C it is identical and equal to 0.06 mg/cm^2 h.

Investigation of the strength and plastic characteristics of ST-4 titanium alloy (the system Ti-Al-Zr-Sn-Fe) has shown [1] that this alloy displays a high degree of heat resistance at 850°C together with satisfactory plasticity. There is no literature which gives information on this heat resistance. In conjunction

with this, structural-kinetic investigations concerning the oxidizability of this alloy in air were conducted at 600-1000°C for 25 h. For the purpose of further increasing its heat resistance, we conducted an investigation into the development of protective coatings. The methods of preparation of the samples and the investigations of the kinetics of oxidation have been described previously in work [2].

Coatings with an Si and Mo–Si base were studied for protection against high temperature gas corrosion. The coatings were produced by thermal diffusion in a vacuum of 10^{-4} Torr. During siliconizing the samples were annealed in a powder of chemically pure Si at 1200°C for 4 h. To obtain a Mo–Si coating, the samples were annealed first in molybdenum powder at 1100°C, and then in silicon powder at 1300°C for 10 h. The samples with coatings were oxidized in air at 800 and 1000°C for 25 h.

Results of experiments and their discussion. The heat resistance of ST-4 alloy at 600-800°C is quite high while at 900-1000°C it decreases sharply; beginning at 950°C, the rate of ST-4 oxidation exceeds the rate of oxidation of non-alloyed titanium (at 1000°C for ST-4 it equals 5 mg/cm^2 h, while for Ti it is 3.5 mg/cm^2 h). Figure 1 depicts the oxidation curves for ST-4 samples and samples with Si and Mo–Si coatings at 1000°C.

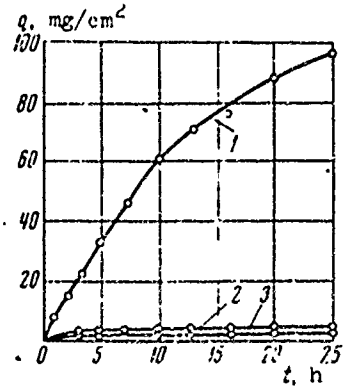

Fig. 1. Kinetic curves showing oxidation in air at 1000°C for ST-4 alloy before and after coating. 1 - without coating; 2 - with Mo + Si coating; 3 - with Si coating; g - weight increment, t - time.

Electron diffraction analysis of the scale, obtained during the oxidation (1000°C) of the sample, has shown that it is composed of TiO_2 and an insignificant amount of γ-Al_2O_3 and ZrO_2;

metallographic analysis did not detect a layer saturated with oxygen, where there is such a layer on titanium. The low heat resistance of ST-4 alloy at 1000°C in comparison with titanium can be explained by the insufficient stability of SnO_2 at this temperature [3]. Besides, the heat resistance of all titanium alloys, including ST-4, decreases significantly in the temperature interval of $\alpha \rightarrow \beta$ transformation, as has been noted previously in numerous works [4-7].

As has been shown by our research and that of other authors, the question of increasing the heat resistance of α-titanium alloys by means of alloying up to the heat resistance level of Ni-Cr alloys has not been satisfactorily resolved. A significant decline in oxygen soluability (and, probably, nitrogen) in titanium is achieved by the multi-component alloying of titanium which stabilizes α, as well as β-titanium. This is supported by metallographic analysis and the dependence of microhardness on the depth of oxygen penetration in β-Ti [4]. Experiments investigating the kinetics of interaction between oxide film, consisting of rutile TiO_2 on iodized titanium, have shown that upon annealing in a vacuum at 10^{-7} Torr oxygen transforms completely into a solid solution. The amount of absorbed oxygen is determined by the weight method, while the phase composition of the film is determined by the X-ray method [8]. The experiments showed the TiO_2 film on the boundary with titanium to be unstable: TiO_2 decomposes due to the soluability of oxygen in titanium. In alloys (particularly with Al) such active interaction of TiO_2 does not occur for the following reasons: 1) the components of the alloy which increase the bonding force in the alloy decrease the oxygen diffusion coefficient 2) the presence of an oxide γ-Al_2O_3 (or ZrO_2) on the boundary between the alloy and TiO_2 retards the diffusion of oxygen towards the alloy's surface and, to a known degree, insulates TiO_2 contact with this surface.

In addition to the effect of the high soluability of oxygen in titanium, $\alpha \rightarrow \beta$ transformation has a great effect on the rate

of oxidation of titanium and its alloys. Aluminum additives increase the temperature of $\alpha \rightarrow \beta$ transformation by 70-100° but cannot eliminate it. Besides, large amounts of aluminum decrease the melting point and increase the brittleness of alloys. Therefore, increasing the heat resistance of alloys while preserving their heat resistant and plastic properties is possible only by using coatings which form finite solid solutions with the alloys while their components form, on the outer surface, oxide films whose oxide lattices consist of tightly packed oxygen ions. Only these types of films will be effective in obstructing the diffusion of oxygen towards the alloy-coating boundary. In addition, octahedral and tetrahedral empty vacancies in these packings (in which cations are located) are extremely small. For example, an octahedral vacancy can contain a cation with a diameter of ~1.12Å. Thus, large cations require high activation energy of diffusion through such oxide lattices. The heat resistant coating must also block the diffusion of titanium and alloy components through the coating layer which is achieved by producing in the coating compounds with strong chemical bond between their atoms.

Coatings	Oxidation	Data for phase analysis of coatings	
		Electron diffraction analysis	X-ray analysis
Si	-	-	Ti_5Si_3 + several lines of TiSi, $TiSi_2$
	+	TiO_2 + several weak lines	TiO_2 + Ti_5Si_3 + an insignificant quantity of TiSi, $TiSi_2$
Mo-Si	-	-	$MoSi_2$ + Mo_5Si_3 + several weak uninterpreted lines
	+	SiO_2	$MoSi_2$ + Mo_5Si_3 + additional lines

Along with this, Si and Mo–Si were selected to produce heat resistant coatings. The table gives the phase composition of the coatings before and after oxidation according to the data of electron diffraction and X-ray analysis. The mean values of the rates of oxidation of coated samples of ST-4 are given below.

	v 800°, mg/cm^2 h	v 1000° mg/cm^2 h
ST-4 without coating	from 0 to 25 h: 0.043	up to 5 h: 7.38 from 5 to 25 h: 3.02
ST-4 Si - coating	up to 5 h: 0.014 from 5 to 25 h: 0.0001	up to 5 h: 0.296 from 5 to 25 h: 0.061
ST-4 Mo–Si coating	up to 5 h: 0.05 from 5 to 25 h: 0.004	up to 5 h: 0.688 from 5 to 25 h: 0.085

The Si-coating consisted, judging by the data of X-ray phase and micro-X-ray-spectral analysis (Fig. 2) mainly of the compound Ti_5Si_3 and traces of TiSi, $TiSi_2$, while the Mo–Si coating consisted mainly of the compound $MoSi_2$ and Mo_5Si_3.

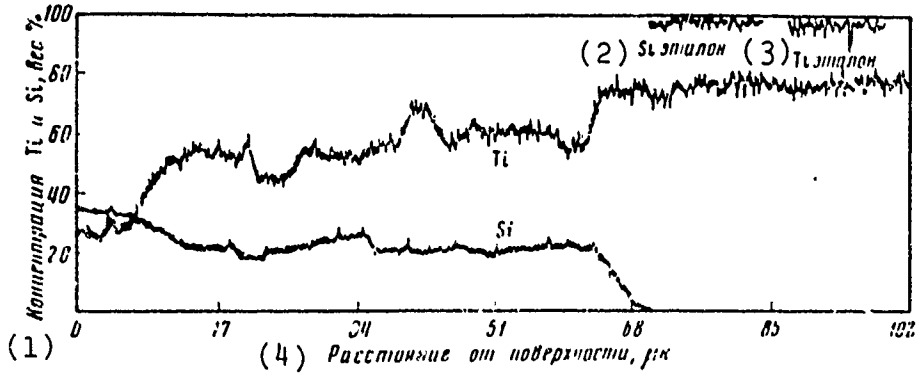

Fig. 2. Distribution of Ti and Si in a siliconized ST-4 sample.
KEY: (1) Concentration Ti and Si/wt. %; (2) Si-standard; (3) Ti standard; (4) Distance from surface, μ.

The silicon coatings display the greatest amount of heat resistance precisely because of the Ti_5Si_3 compound: at 800°C the heat resistance of the sample with the coating is 400 times while at 1000°C it is 50 times greater than that of a noncoated sample.

Samples having a Mo–Si coating have an oxidation rate at 1000°C 40 times less than that of noncoated samples.

The high degree of heat resistance of Ti_5Si_3 coatings in the presence of mainly TiO_2 films on their outer surface, which is not a protective coating, is explained by 1) the high energy of the bond between the Ti and Si atoms in the Ti_5Si_3 lattice, whose heat of formation equals -18.4 ± 1.5 kcal/g·atm [9], as result of which a high activation energy is necessary for the breaking of this bond and the transfer of titanium ions into the TiO_2 lattice 2) the absence of interaction between TiO_2 and Ti_5Si_3. The predominant formation of TiO_2 and not SiO_2 on the outer surface is explained by the high heat of formation of TiO_2 (112.8 kcal/mole) in comparison with SiO_2 (105.0 kcal/mole) [10].

It is interesting to note also that silicide coatings decrease the oxidation rate of ST-4 alloy at 800° by a factor of 70 in comparison with the oxidation rate of an alloy composed of 80% Ni + + 20% Cr, while their rates are identical (0.06 mg/cm^2·h) at 1000°C.

Using electron diffraction, we detected on the surface of a sample coated with Mo + Si and oxidized at 800° and 1000°C for 25 h, the SiO_2 phase in the form of α-cristobalite. The same SiO_2 was found by electron diffraction during oxidation of $MoSi_2$ in air (750–1500°C) [11].

In this way, it is possible with the help of such coatings to increase the heat resistance of titanium alloys up to the level of heat resistance of Ni–Cr alloys and to eliminate almost completely the effects of oxygen soluability and α → β transformation on the oxidation rate of these alloys.

Conclusions. 1. We conducted structural-kinetic investigation of the oxidizability of titanium alloy ST-4 with and without protective coatings.

2. Ti_5Si_3 coatings display the best protective properties against gas corrosion at 800-1000°C. The heat resistance of ST-4 alloy with Ti_5Si_3 coating at 800°C is 70 times greater than that of an 80% Ni + 20% Cr alloy.

3. By using these coatings, the adverse effects of high oxygen soluability (and nitrogen) and $\alpha \rightarrow \beta$ transformation on the oxidation rate of titanium and its alloys can be eliminated.

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